A STUDY ON STRUCTURAL PROPERTIES OF HYDROXYAPATITE-ZIRCONIA COMPOSITES

A thesis submitted for partial fulfilment of the requirement for the degree of Bachelor of Technology under the guidance of Professor SUDIP DASGUPTA

By

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CERTIFICATE

This is to certify that the project entitled "**A STUDY ON STRUCTURAL PROPERTIES OF HYDROXYAPATITE-ZIRCONIA COMPOSITES**" submitted by **SANKALP AWASTHI** is a genuine work performed by him under my guidance required for the **Bachelor of Technology** degree in **Ceramic Engineering** at **National Institute of Technology, Rourkela.**

To the best of my knowledge, this thesis is very authentic and none of its matter has been submitted anywhere else for the award of degree or diploma.

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ABSTRACT

For the project work, hydroxyapatite-zirconia composite with varying zirconia composition were prepared and subsequent characterization was performed. Hydroxyapatite was prepared by using calcium nitrate and di-ammonium hydrogen phosphate, while zirconia was prepared by using zirconia oxychloride and ammonium hydroxide solution. Both hydroxyapatite and zirconia powders were prepared by precipitation method. Zirconia was added to the extent of 5, 10 and 20 weight percent, the mixture was milled for 4 hours and then consolidated into pellets and sintered at 1200°C for 4 hours. The XRD analysis showed the presence of β-TCP (tricalcium phosphate) in the sintered pellets, due to the decomposition of Hydroxyapatite. The study shows that the properties, like bulk density, Vicker's hardness and bi-axial flexural strength, of hydroxyapatite can be improved by the addition of zirconia. This makes it suitable for application in load bearing bony sites where only hydroxyapatite might fail under load.

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1. INTRODUCTION

Bioceramics are an important class of ceramic materials which produce no harmful immunogenic reactions with living tissues. Important classes of bioceramics are bio-inert (having no reactions with the living tissues, e.g. alumina (Al_2O_3)), bio-active (hydroxyapatite, bio-glass), bio-resolvable (tricalcium phosphate) and porous bio-metals (metal alloys coated with hydroxyapatite). These are used generally for the repair and reconstruction of damaged tissues of the skeletal system, which include dental implants, bone scaffoldings, bone plates, joint replacements and bone replacements. [1, 2]

With the ongoing developments and researches in medical and ceramics, we have found a vast use of bioceramics. This aims at improving the health and life-expectancy of human tissues and bones. Bone ailments are very common, and bioceramics can acutely solve this problem in both young and ageing human populace. Researchers are finding new ways to improve the structural and chemical properties of bioceramics, so as to make them more compatible with human body and improve their usage for the treatments. Studies are ongoing to make bioceramics as imitable with the human tissues and bones as possible. [3. 4]

Apatites are phosphate minerals having varying Ca/P ratios which are produced and used by biological microsystems. These are mostly found in human bones and teeth as Hydroxyapatite and Fluoroapatite.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), also referred as HA is a naturally occurring calcium apatite mineral, found in animal bones, having Ca/P=1.66. It is a nontoxic, biocompatible, osteoconductive, non-immunogenic bioceramic and forms direct bonds with living tissues. All the apatites have crystal structures and chemical properties similar to human bones, and HA is the most biocompatible of the lot. HA is generally used as coating on bone implants and scaffolds because of its excellent biocompatibility and osteoconduction,

but cannot be used directly for bone replacement because of its poor mechanical properties like fracture toughness and hardness. [5] Therefore its application right now is limited to non-load bearing areas. Studies are ongoing to improve the load bearing strength of HA, so as to improve its mechanical properties and subsequent usage in medical applications. [6, 7]

Zirconia (ZrO_2) is an important ceramic material which possesses very good mechanical properties like fracture toughness and hardness. Apart from these, ZrO_2 is bio-inert and can be used for femoral head replacement prostheses [8, 9] and in dental restorative materials [10]. Its aesthetic (color and texture) and high wear resistance makes it ideal for usage in bioceramics. Apart from these, zirconia is also used as an additive to improve the mechanical properties of various ceramics like alumina and mullite [10, 11].

A bone transplant material requires two main criteria, bioactivity and material toughness. Hydroxyapatite illustrates strong bioactivity but shows very poor wear resistance and toughness whereas zirconia is bio-inert, but has excellent wear and fracture toughness. Studies are ongoing to produce hydroxyapatite-zirconia composites that show desirable bioactivity and structural properties similar to that of natural bone. A major problem faced is the thermal decomposition of hydroxyapatite during sintering (this produces TCP, which shows poor bioactivity) and the reaction between the zirconia phase and the hydroxyapatite phase [8, 11]. Also we need to find the optimum measure in which both the materials must be mixed to produce desired properties. The current project work shows how varying percent of zirconia affects the physicochemical and mechanical properties of hydroxyapatite after sintering.

2. LITERATURE REVIEW

Apatite minerals have crystallographic structure and chemical composition which bears good resemblance to that of human bones. Of all the crystallographic minerals, Hydroxyapatite, with a Ca/P ratio of 1.67, matches the bioactivity of bone tissues the most, and hence is used for the treatment of skeletal deformations and implant coatings. However, its application is limited to areas where load bearing strength is not a high priority [1, 3, 14, 18]. Hydroxyapatite cleaves along {0001} and {0010} planes, and thus has very poor wear resistance, fracture toughness and load bearing capacity [2]. Therefore, only middle ear bones (ossicles) transplant and metallic implant coatings are the main areas of application of hydroxyapatite [14]. To achieve the full potential of Hydroxyapatite, research is ongoing to improve its mechanical properties like hardness, bi-axial flexural strength and CCS [19]. This is achieved by designing HA-ceramic composites, with varying chemical and quantitative composition. Ceramic materials are used in the composites because of their desired mechanical properties and bio-inertness. The properties required are bio-inertness, bio-resolvability, hardness, low tensile strength and high compressive strength [1]. Furthermore, ceramic oxides can be chemically synthesised very easily, and with high purity. Ceramic oxides are mostly used in dynamically changing environments requiring high wear resistance as refractories, space craft coatings and high temperature engines. Our body is akin to these systems in the respects of environmental degradation and wear. Constant osteablastic and osteoclastic activities ensure that the implant undergoes high working stress and degradation. As soon as body fluids come in contact with the implant surface, immunogenic cells start their actions on nanoscale, which initiate the degradation of the implant surface. A layer of protein soon covers the implant surface, and the interchange of ions and generation of osteoclasts starts. The rate of decomposition depends on the surface morphology of the powder, its wettability, surface

charge accumulated and the porosity of the coating. We require a bioresolvable coating here, as if toxins are released as products of this reaction, the body might undergo huge harms. A desirable surface provides for an excellent interface for Macrophage fusion and collagen genesis. Thus the chemical nature of the bio-implant plays an important role in determining the success of the transplant and its structural properties [1,2,3].

Bioceramics are compatible with the living tissues. This is a result of the dynamic exchange between the body environment and the ceramic. Bioceramics generally have ions like Ca2+, K+, Mg2+, Na+ which are also present in the body tissues and hence are acceptable, or ions like Al3+ and Ti2+ which are bio-inert and produce no obstruction to the body functions. Bio-inert ceramics, like alumina, alumina-zirconia, zirconia, etc. show excellent structural properties and have been used as dental transplants. However, their bio-inertness has prevented their extensive use in the field of bone transplants and/or replacements. We require a ceramic material which exhibits excellent bioactivity and has mechanical properties similar to that of human bone, so that it could be eventually replaced by natural bone tissues and interacts freely with the body environment. Apatite minerals come into play here, particularly Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. They provide for an excellent surface for interaction between body tissues and transplant to occur, hence generating natural bone tissues and collagen, which will replace the bone transplant gradually [16, 20]. Other bioactive biomaterials include A-W glass ceramics, bio glass and bioactive glasses. The main problem with the usage of Hydroxyapatite lies in its crystal structure. Synthetic HA cleaves very easily because of its layered structure and hence has poor wear resistance and fracture toughness. This is a serious limitation for the clinical use of HA. They can be used as coatings on metallic implants to provide for a surface onto which bio activity can occur, but this hasn't been very successful because of non-conformal matrix reactions between the implant and bone tissues.

Zirconia is a bio-inert ceramic oxide, and is usually used as a reinforcement in ceramic composited. Tetragonal zirconia gives good fracture resistance, has very low thermal expansion coefficient and has very high hardness. This makes up for an excellent reinforcement for HA, and can enhance its structural properties [15].

It is found that HA-Zirconia composites, fired in the range of 1200-1350 C, give a highly dense body having hardness and strength higher than the pure HA bodies. This paved way for researches to incorporate HA-Zirconia composites for clinical trials [21, 23]. A main problem with the sintering process is that TCP (Ca/P=1.5) starts forming above 1300 C, which is undesirable because of its poor bioactivity. This can be resolved by sintering the ceramic body not above 1200 C, by using High Frequency Induction heat sintering at 1125 C or by addition of small amounts of CaF_2[20].

For the current project, the structural properties of HA-Zirconia composites were studied. The pellets were prepared with varying weight % of zirconia, viz 5%, 10% and 20%, and pressed green bodies were sintered at 1200 C. Characterization of the sintered bodies was done to find out the bulk density, apparent porosity, Vicker's Hardness and Bi-axial flexural strength.

3. EXPERIMENTAL PROCEDURE

3.1. Preparation of Hydroxyapatite

Hydroxyapatite was synthetically prepared by precipitation of Calcium Nitrate tetrahydrate with diammonium hydrogen phosphate, taken in the molar ratio of 1.67, under pH of 10. The reaction is

$$10Ca(NO_3)_2.4H_20 + 6(NH_4)_2HPO_4 + 8NH_4OH = Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 20H_2O$$

Steps taken for the preparation of HAp are the following:-

1. 11.75 gm of calcium nitrate tetrahydrate was dissolved in 60 ml water. To obtain a clean solution, approximately 5 ml of dilute nitric acid was added.
2. 4 gm of diammonium hydrogen phosphate was mixed in distilled water and the solution was mixed with constant stirring.
3. Dropwise 25 % ammonia solution was added to this mixture till a white precipitate started to form. The mixture was then stirred for 3 hours at 60 degree centigrade.
4. The solution was allowed to stand for 24 hours.
5. After sedimentation of the precipitate, the clean solution was decanted off and the precipitate was removed by filteration.
6. 3.89 gm of impure Hap was washed and dried for 24 hours.
7. The Hap was washed and centrifuged 3 times till the pH value was recorded as 7.
8. The powder was dried for 24 hours. The final weight of the powder left was 2.97 gm.
9. The dried powder was then calcined at 600 C for 4 hours.
10. XRD analysis of the powder was done to find the phases present.

3.2. Preparation of Zirconia

Zirconia is prepared by the action of ammonium hydroxide on zirconia oxychloride. The reactants were taken in the ratio 1:1.

Steps taken for the preparation of zirconia hydroxide from zirconia oxychloride are the following:-

1. 5.75 gm of zirconia oxychloride was dissolved in 100 ml distilled water to get a clear transparent solution.
2. The solution was made to react with 25 ml of 25 % ammonia after adding dropwise ammonia solution with constant stirring. Care was taken to assure that the pH was maintained at 8.
3. The precipitate was allowed to stand for 24 hours.
4. To obtain pure zirconium hydroxide, the residual solution was subjected to centrifugation at 8000 rpm for 5 minutes. The powder obtained was washed repeatedly to make the pH=7.
5. The powder was then calcined at 600 C for 4 hours to obtain monoclinic zirconia.
6. XRD analysis was done to find the phases present in the powder.

3.3. Preparation of HA-Zirconia composited

Zirconia powder was taken as 5%, 10% and 20% by weight of hydroxyapatite and pot milled for 4 hours using zirconia balls as grinding media. To make sure that the pellets do not break after pressing, 10% PVA binder was added in tune of 1% by weight of the pellets. The binder was mixed in a mortar pestle, and the powder mass was grinded and sun dried for 1 hour. This was followed by pressing at 3 tons with 120 seconds of holding time. The die punch used was of 8mm diameter.

3.4. Sintering

The pellets were then sintered in the furnace at 1200 C for 4 hours. Alumina plates were uses as base for the sintering of pellets. Only pellets showing no visible cracks were considered for further characterization.

3.5. Characterization

3.5.1. X-Ray Diffraction

Philip X-Ray Diffractometer (Holland, PW 1730) was used for the purpose of XRD of the pellets. The diffraction was done via Nickel filtered Cu Kα radiation (λ = 1.5406 A°) at 10 kV and 30mA having a scan range (°2 θ) of 20-80° for both HA and ZrO_2 powders and all the composites prepared.

3.5.2. Bulk Density and Apparent Porosity

Bulk density and apparent porosity was calculated using Archimedes principal. The weight of pellets (Dry Weight= D) were taken and recorded. The pellets were then kept under boiling water till no bubbles come out of the pellets. The heating was stopped and the pellets were soaked for 1 hour. Afterwards, the soaked weight (W) and suspended weights (S) were calculated. The bulk density and apparent porosity of the pellets were calculated using the formula:

$$\text{Bulk Density} = \frac{Dry\ Weight}{Soaked\ Weight - Suspended\ Weight} = \frac{D}{W-S}$$ (Density of liquid not included as water was used as soaking media)

$$\text{Apparent Porosity} = \frac{Soaked\ Weight - Dry\ Weight}{Soaked\ Weight - Suspended\ Weight} = \frac{W-D}{W-S}$$

3.5.3. Vicker's Hardness Test

Before testing for hardness, the pellets were polished properly using silicon carbide paper for 30 minutes. This was done in order to enhance the appearance of the indent and make sure that the indented surface is even. A load of 0.3 kgf was applied for indent, and microscope was then focussed to measure the diagonal length of the indent. Vicker's Hardness is given by the formula:

$H_v = 1.854 * \frac{F}{d*d}$, where F is the force of the indent, given in kgf and d is the diameter of the indent, calculated in mm.

3.5.4. Bi-axial Flexural Strength

Before testing for the bi-axial flexural strength, the diameter and thickness of the pellets were recorded. The testing was done via UTM machine. The pellets were kept on a ring width wise and a constant extension force was applied on them. The instrument measured the maximum load at the fracture point. Bi-Axial Flexural Strength was measured by the formula:

Strength = $\frac{2*F}{\pi*d*t}$, where F is the force at the breaking point of the pellet, d is the diameter of the pellet and t is the thickness of the pellet.

4. RESULTS AND DISCUSSIONS

4.1. Results

4.1.1. Identification of phase in the XRD samples of Hydroxyapatite and Zirconia

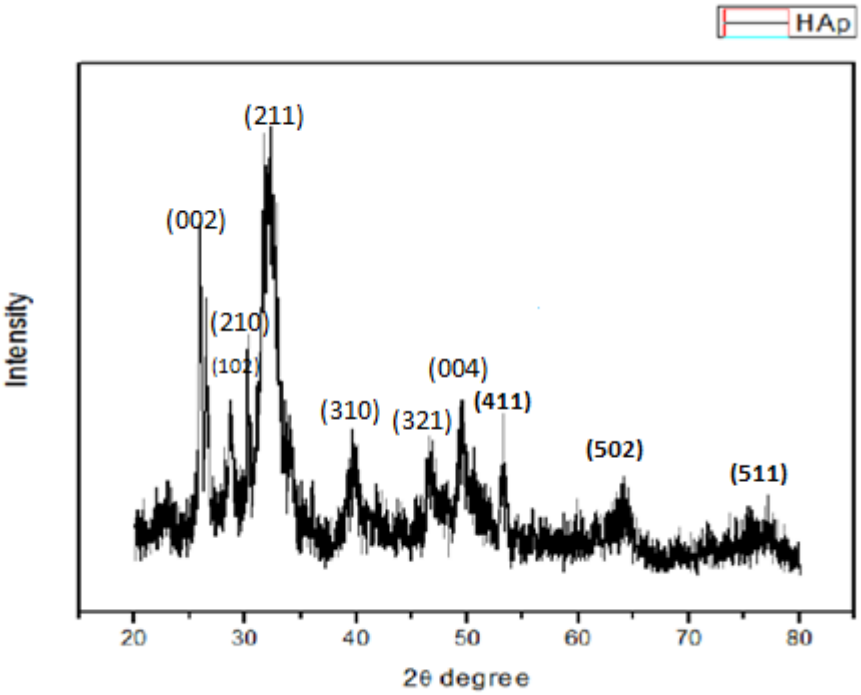

Fig 1. XRD graph of Hydroxyapatite powder

Figure 1 shows the XRD plot for hydroxyapatite powder calcined at 600 C. The powder obtained has mainly Hydroxyapatite phase, as only HA powder was precipitated during the reaction.

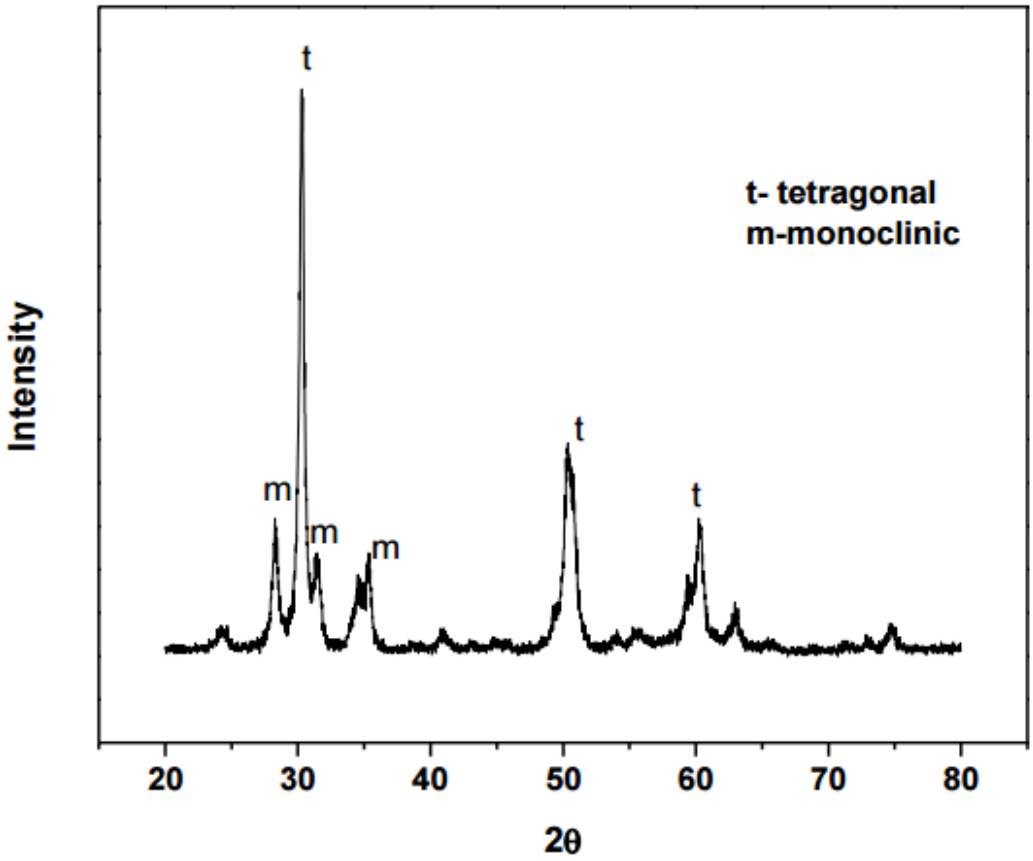

Fig 2. XRD Graph of Zirconia Powder

The plot of XRD analysis of zirconia powder after calcination at 600 C is shown in figure 2. The plot shows that both monoclic and tetragonal phases were present in the Zirconia powder.

4.1.2 Identification of the XRD pattern of Hydroxyapatite-Zirconia pellets sintered at 1200 C.

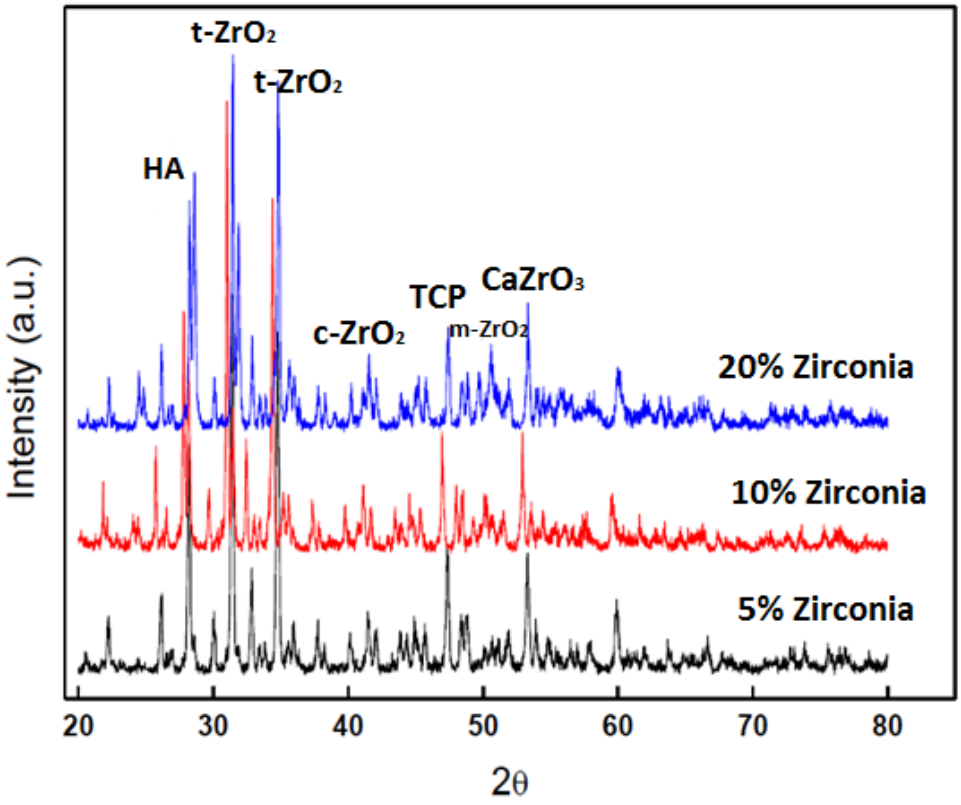

Fig. 3. XRD plot of HA-Zirconia composites sintered at 1200 C

The XRD plot of fig. 5 shows that the phases present in HA – Zirconia composite after sintering at 1200 C were hydroxyapatite, tricalcium phosphate, tetragonal zirconia, monoclinic zirconia, cubic zirconia and $CaZrO_3$.

4.1.3. Bulk Density and Apparent Porosity Analysis of the sintered pellets.

Pellet Type	Bulk Density	Apparent Porosity
5% - A	3.55	8.77%
5% - B	3.54	9.02%
5% - C	3.47	9.18%
10% - A	3.36	12.36%
10% - B	3.38	11.56%
10% - C	3.33	12.34%
20% - A	3.31	11.72%
20% - B	3.29	11.78%
20% - C	3.31	11.70%

Table 1. Bulk Density and apparent porosity values for different HA-Zirconia composite pellets

The trend observed in the bulk density values was that they decreased with the increase in the zirconia content of the pellet, whereas the apparent porosity values increased with increase in zirconia percentage. The highest BD value of 3.55 g/cc was observed in 5% zirconia loaded sample, whereas the lowest value was 3.29, observed in 20% zirconia loading. Similarly, the highest AP value was 12.34% observed in 20% zirconia loading, while lowest was 8.77% for the 5% zirconia loaded sample.

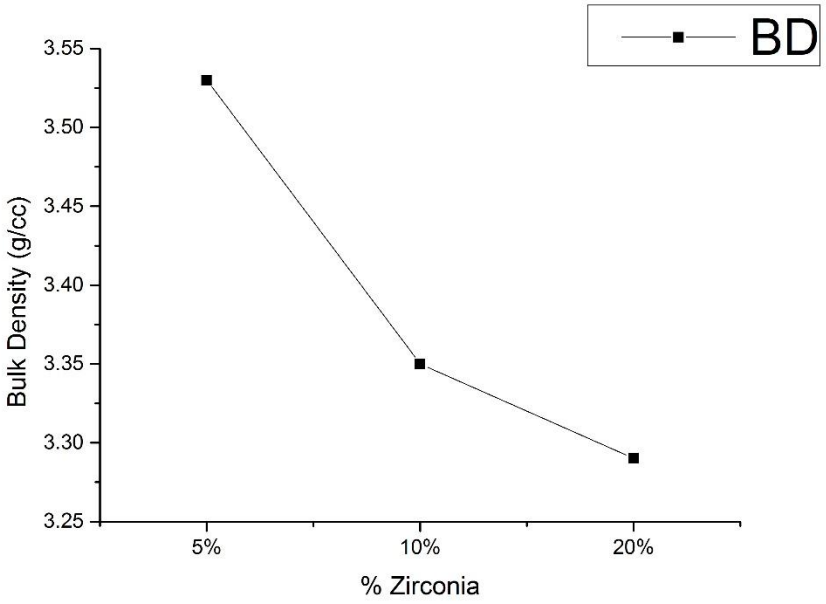

Fig. 4. Variation of average bulk densities with the zirconia loading. 1, 2, and 3 on x axis respectively indicate 5%, 10% and 20% loading.

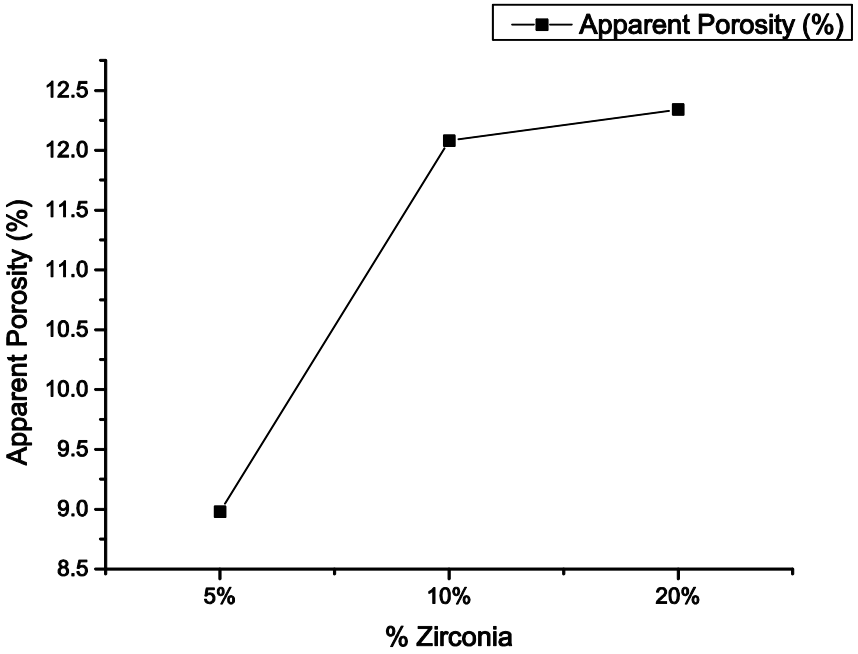

Fig. 5. Variation of the average Apparent Porosity with the Zirconia loading

4.1.4. Vickers Hardness Test

Sample	Vicker's Hardness (Hv)(MPa)
5% - A	392
10% - A	301.6
10% - B	297.8
20% - A	219.1
20% - B	278.2

Table 2. Hardness values of different HA-Zirconia composites

As evident from table 2, the hardness of 5% zirconia loading was highest (392 MPa) while 20% loading gave the least hardness (219.1 MPa).

4.1.5. FESEM analysis of the pellets

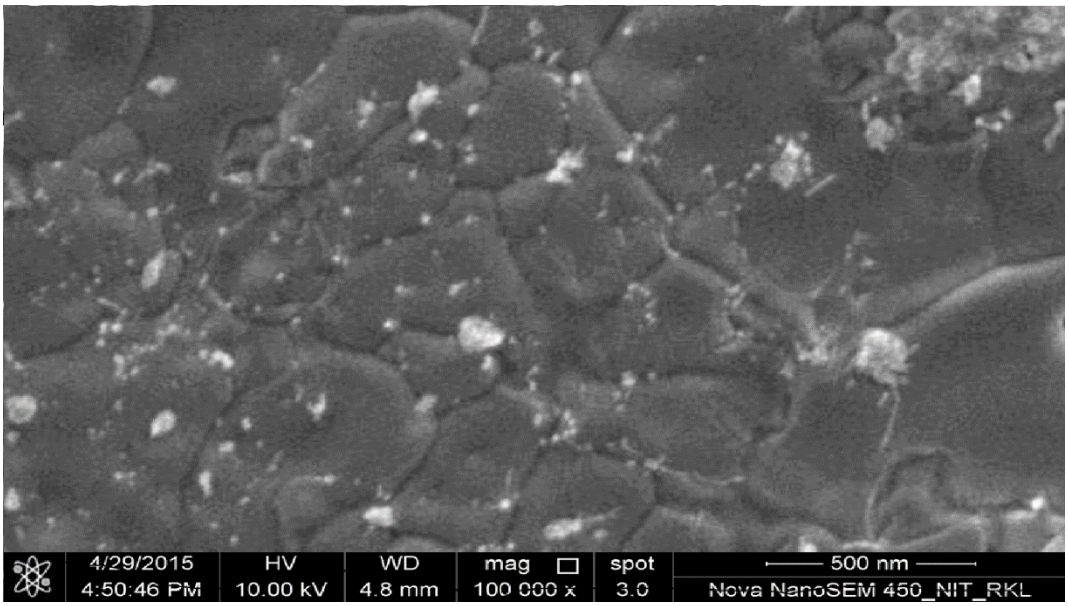

Fig. 6. FESEM image of 5% Zirconia loading.

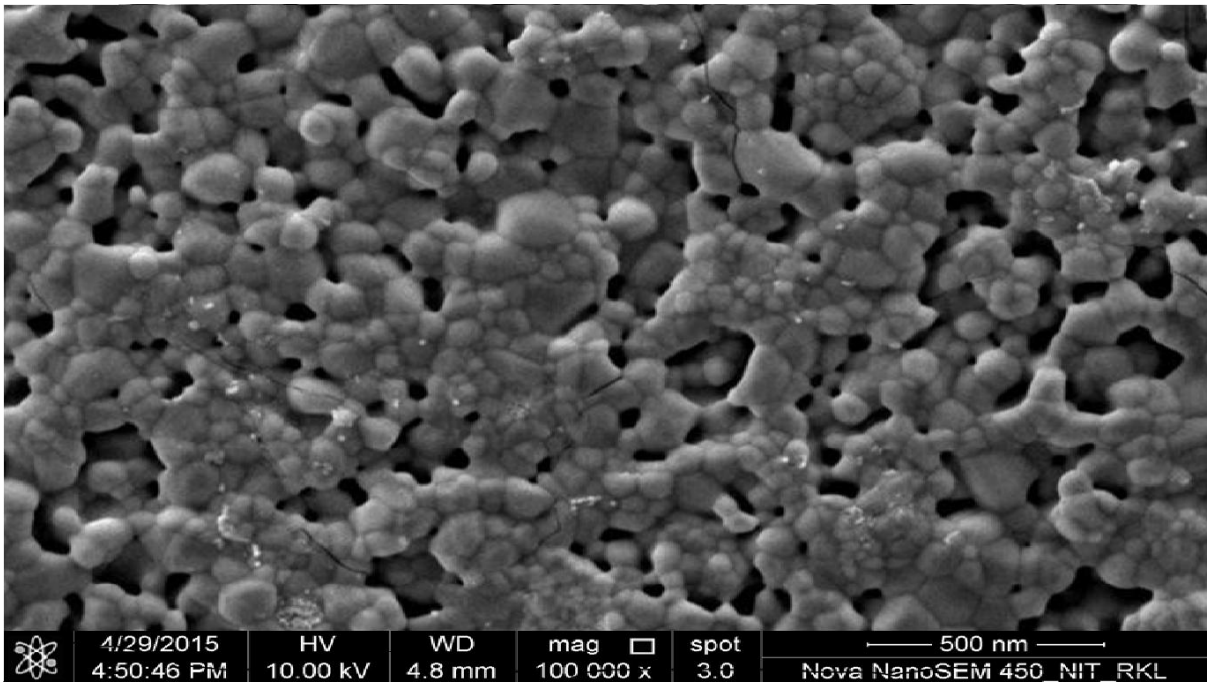

Fig. 7. FESEM image of 10% Zirconia loading

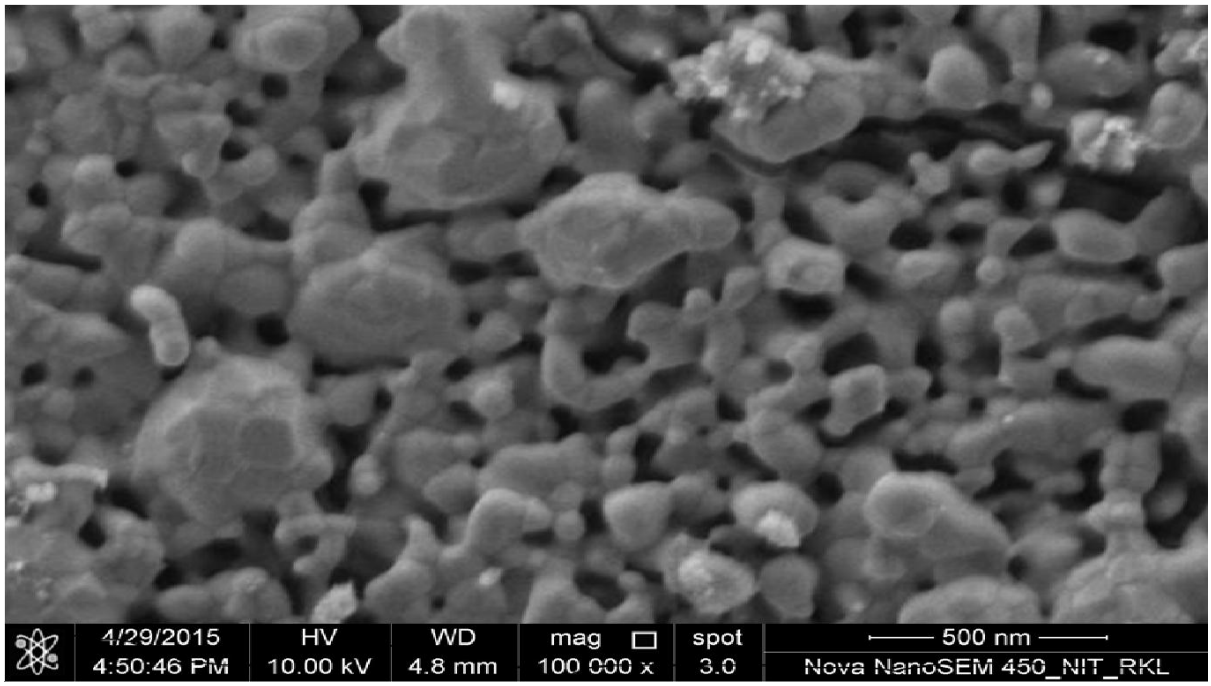

Fig. 9. FESEM of 20% Zirconia loading

As evident from the BD and AP data, the FESEM images show pores in 20% and 10% samples, while the 5% samples are relatively dense.

4.1.6. Bi-Axial Flexural Strength

Sample	Bi-Axial Flexural strength(MPA)
5%	20.21
10%	23.11
20%	11.78

Table 3. Bi-Axial flexural strength of different HA – Zirconia composites

The above table shows the different values of Bi-Axial flexural strength of different HA-zirconia composites. An anomaly occurred here, as the 10% sample is showing the highest value instead of the 5% sample.

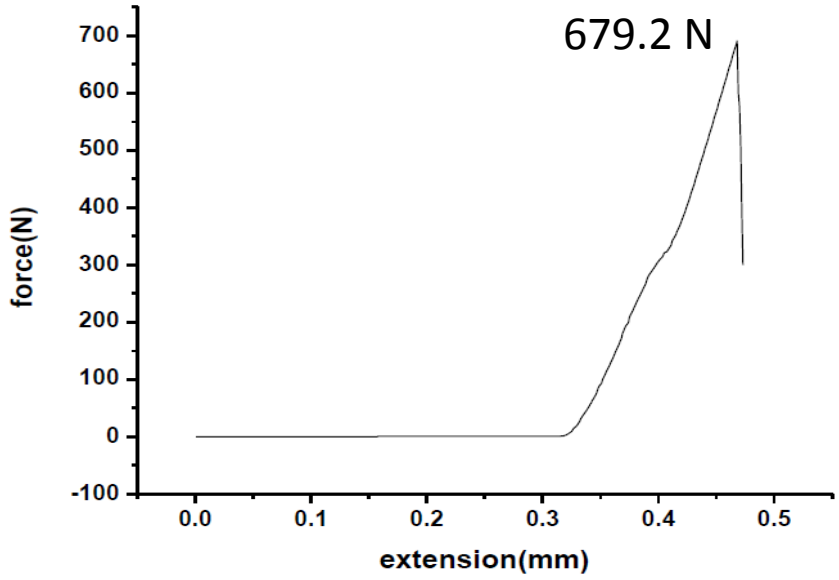

Fig. 11. The force – extension graph of 5% Zirconia Pellet.

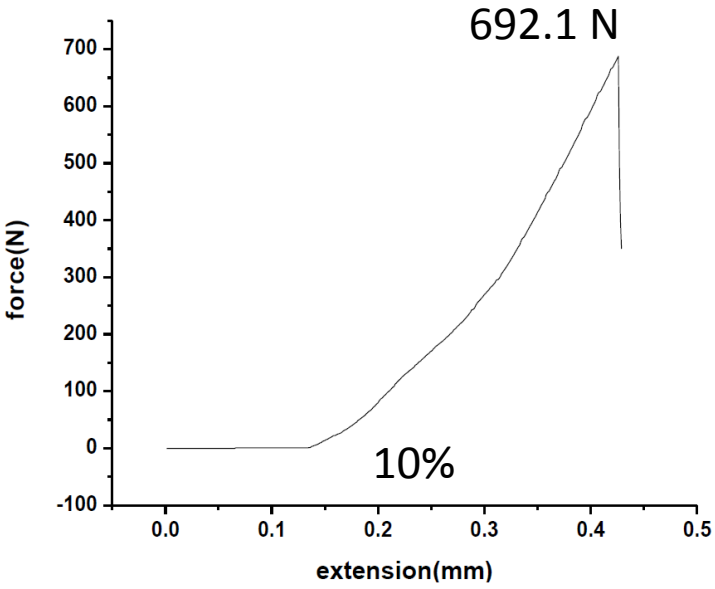

Fig. 12. The force - extension graph of 10% Zirconia Pellet

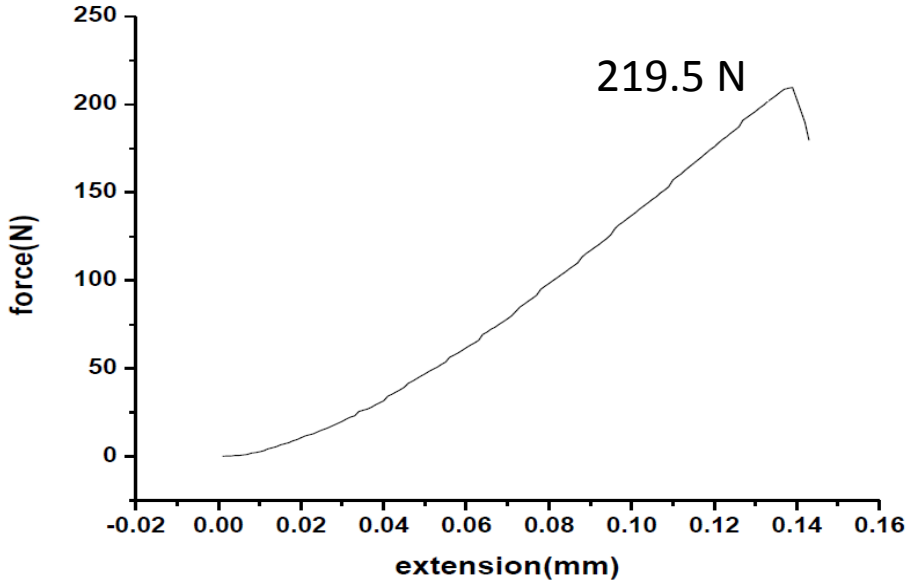

Fig. 13. The force-extension graph of 20% Zirconia Sample

4.2. DISCUSSION

Only phase pure Hydroxyapatite powder was obtained in the preparation stage. This is because only HA was precipitated in the reaction

$$10Ca(NO_3)_2.4H_20 + 6(NH_4)_2HPO_4 + 8NH_4OH = Ca_{10}(PO_4)_6(OH)_2 + 20NH_4NO_3 + 20H_2O$$

Zirconia was obtained as $Zr(OH)_4$, but the powder was calcined to get pure zirconia.

$$ZrOCl_2 + 2NH_4OH = Zr(OH)_4 + 2NH_4Cl$$

$$Zr(OH)_4 \rightarrow ZrO_2 + H_2O$$

TCP was observed as a phase in the sintered pellets. This TCP came as a result of the degradation of HA. Also in high temperature conditions, Ca^{2+} ion, released by HA, reacts with Zirconia to form cubic Zirconia and $CaZrO_3$. This adversely affects the densification process, as the Zirconia attaches itself to the HA grain boundary, and stops the grain boundary diffusion during sintering. Thus with an increase in the percentage of zirconia loading, the bulk density and apparent porosity decreases. This subsequently affects the hardness and bi-axial flexural strength of pellets.

The anomaly in the value of bi-axial strength of 10% pellet can be attributed to the transformation toughening showed by zirconia, which has superseded the low bulk density of the pellets, thereby showing a higher value than the 5% pellet.

5. CONCLUSION

The aim of this project was to study the effect of zirconia loading on the structural properties of hydroxyapatite-zirconia sintered pellets. We observed that the bulk density decreased with the increase in the percentage of zirconia, and the 5% loaded sample showed the highest bulk density and lowest apparent porosity after sintering at 1200 C for 4 hours. This is due to the fact that increased zirconia percentage hampered the grain boundary diffusion of hydroxyapatite, thus affecting the densification process. The 5% loaded sample showed the highest hardness, while the 10% sample showed the highest flexural strength. This anomaly was due to the transformation toughening of zirconia. To further optimize the mechanical properties of the pellets, microstructure of HA and zirconia needs to be tailored. This can be accomplished by using nano sized HA and tetragonal zirconia particles. Further studies can be done on the bioactivity and osteoconductivity of the samples, paving way to further research for the tailoring of HA-zirconia composites that fulfil the load bearing applications as required by medical implants.

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